UNIVERSITY OF PENNSYLVANIA

ACTIVITY COEFFICIENTS OF THE ALKALI HALIDES

STUART DUNSHEE DOUGLAS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Herbert S. Harned, under whose direction and guidance this work was done, and to Mr. Geoffrey M. James for his valuable assistance in taking the readings.

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THE ACTIVITY COEFFICIENTS OF THE ALKALI HALIDES

INTRODUCTION

The activity coefficients of alkali halides have been studied by a number of investigators,[1] by measurements of the cells

$$Ag\,|\,AgCl\,|\,MCl(m)\,|\,M_xHg\,|\,MCl(m_0)\,|\,AgCl\,|\,Ag$$

By this means, MacInnes and Parker and MacInnes and Beattie have determined the activity coefficients of potassium chloride and lithium chloride in concentrations ranging from 0.01 to 1 M. and from 0.01 to 3.0 M., respectively. Allmand and Pollack have measured the activity coefficient of sodium chloride by a similar cell in dilute and concentrated solutions, and Pearce and Hart have studied potassium bromide solutions. Furthermore, the activity coefficient of hydrochloric acid is well known, and that of hydrobromic acid has been recently determined by Livingston.[2]

The only investigation of an iodide has been carried out on hydriodic acid by Pearce and Fortsch[3] who obtained accurate results in the low concentration range (0.005 to 0.05 M.). With the idea of making more complete this general study, we have undertaken an investigation of the activity coefficients of concentrated aqueous solutions of potassium and sodium bromide

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[1] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).
MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).
Allmand and Pollack, *ibid.*, **115**, 1020 (1919).
Pearce and Hart, *ibid.*, **43**, 2483 (1921).

[2] Livingston, *J. Am. Chem. Soc.*, **48**, 45 (1926).

[3] Pearce and Fortsch, *J. Am. Chem. Soc.*, **45**, 2852 (1923).

and of potassium and sodium iodide, and for this purpose have employed the cells

$$\begin{array}{l} Ag\,|\,AgBr\,|\,NaBr\ (m_2)\,|\,Na_xHg\,|\,NaBr(m_1)\,|\,AgBr\,|\,Ag \\ Ag\,|\,AgBr\,|\,KBr(m_2)\,|\,K_xHg\,|\,KBr(m_1)\,|\,AgBr\,|\,Ag \\ Ag\,|\,AgI\,|\,NaI(m_2)\,|\,Na_xHg\,|\,NaI(m_1)\,|\,AgBr\,|\,Ag \\ Ag\,|\,AgI\,|\,KI(m_2)\,|\,K_xHg\,|\,KI(m_1)\,|\,AgI\,|\,Ag \end{array}$$

From the examination of the data of the above investigators, we find that when the electromotive forces of these cells are referred to 0.1 M. solutions, the differences in potential at a given concentration between the hydrochloric and hydrobromic acid cells and the potassium chloride and potassium bromide cells were identical within the experimental error up to and including 1.0 M. solutions. This would lead approximately to the conclusion previously suspected by MacInnes and by Harned[4] that the electromotive forces of the individual electrodes or of the individual ions are additive, in the case of these simple electrolytes, when referred to a given standard concentration. The present measurements will serve to supplement the meagre data on this subject. Although by this method, sufficient accuracy has not been obtained to establish such a principle within a fraction of a per cent, they will be shown to indicate that up to high concentrations this principle is approximately valid.

That being the case, these data may be employed for approximately determining the activity coefficients of halides which have not yet been determined and which like hydriodic acid are very difficult to determine in the concentrated solutions without employing the complicated freezing point method.

Further, we have determined the activity coefficient of sodium hydroxide in sodium bromide and in sodium iodide solutions, by means of the cells:

$$\begin{array}{l} H_2\,|\,NaBr(m),\ NaOH(m_2)\,|\,Na_xHg\,|\,NaOH(m_1)\,|\,H_2 \\ H_2\,|\,NaI(m),\ NaOH(m_2)\,|\,Na_xHg\,|\,NaOH(m_1)\,|\,H_2 \end{array}$$

which will serve toward completing the experimental material

[4] MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919).
Harned, *ibid.*, **42**, 1808 (1920).

for the calculation of the activity coefficient of water as electrolyte in these halide solutions, and thus its dissociation.

EXPERIMENTAL

Sodium amalgam was made from mercury which had been purified by passing it in a fine stream through a long column of very dilute nitric acid, drying and three times distilling in a vacuum. A ten per cent solution of high-grade sodium hydroxide was electrolyzed using 70 c.c. of this mercury as the cathode and a platinum foil as the anode, until an amalgam containing approximately 0.10 per cent sodium was formed. This was allowed to run into a highly evacuated Pyrex flask fitted with a stop-cock and constricted side-arm, the latter fused on to a vacuum line, heated gently for some time to drive out all traces of moisture, and finally inverted. After standing for several days to allow any impurity present to rise to the surface, this strong amalgam was run into a similar flask of larger capacity containing 700 c.c. of pure mercury. This diluted amalgam (about 0.01 per cent) was treated as before and placed in such a position that the dropper could be filled directly without contact with air.

Alkali solutions were made from a saturated solution of sodium hydroxide. Since sodium carbonate is insoluble at this concentration, any carbonate present soon formed a crust on the surface leaving the uncontaminated hydroxide below. This was diluted to about ten per cent, and the last traces of carbonate precipitated by adding, drop by drop, a saturated solution of barium hydroxide until barium carbonate ceased to form. Five to ten drops were found to be sufficient. The solution was now analyzed and diluted with freshly boiled, redistilled water, to 0.1 M. strength, fitted with a soda-lime tube and accurately titrated against standard 0.1 M. Hydrochloric acid.

Standard hydrochloric acid solutions were prepared from the constant-boiling acid and were analyzed gravimetrically.

Hydrogen was generated by electrolyzing a 20 per cent solution of sodium hydroxide using a nickel cathode and a platinum anode, conducted through an alkaline pyrogallol solution to re-

move traces of oxygen, then through a saturator containing solution of the same strength as that used in the cell, and finally into the hydrogen electrode chamber of the cell.

The salts used, sodium bromide, potassium bromide, sodium iodide, and potassium iodide, were of the best grade obtainable and were carefully ground and dried before using.

The neutral salt solutions were prepared by weighing out a calculated amount of salt into a weighed flask and adding a slight excess of the appropriate amount of water. They were then boiled under reduced pressure and reweighed, corrections being applied for the loss of water. The solutions could now be transferred to the cell without exposure to air.

The alkali-salt mixtures were made by weighing out a calculated amount of salt into a boiling flask containing a weighed quantity of standard sodium hydroxide solution. This solution was then boiled, reweighed and transferred to the cell in the usual manner.

In making silver-silver bromide and silver-silver iodide electrodes, the technique of Noyes and Ellis[5] was followed. A platinum helix sealed through a glass tube was plated with silver and coated with well-washed silver oxide paste which was then reduced to spongy silver in an electric furnace. The bromide electrodes were coated with silver bromide by making them the anode in a solution of 0.75 N. hydrobromic acid, using a current of ten milliamperes each for two hours. The iodide electrodes were made in a similar way, using a fresh hydriodic acid solution obtained by slowly dropping water on to a mixture of iodine and red phosphorus, passing the evolved hydriodic acid gas over phosphorus to remove any iodine vapor, into a weighed amount of distilled water. This solution was disconnected from the generator from time to time and weighed, until a solution of correct strength was obtained. It was found impossible to keep hydriodic acid solutions for more than twenty-four hours due to oxidation and consequent liberation of iodine.

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[5] Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2532 (1917).

Flowing amalgam electrodes have been successfully used by a number of investigators.[6] They were introduced by Meyer and later by Lewis and his associates[7] who found them to be among the most reproducible electrodes.

The hydrogen electrodes were made in the usual manner by coating with platinum black a piece of platinum foil (3 mm. x 1 mm.) which had been fused to a platinum wire and sealed into a glass tube.

All measurements in an electrically operated thermostat which maintained a constant temperature of 25° C.

The electromotive force measurements were made on a Leeds and Northrup potentiometer, Type K.

ELECTROMOTIVE FORCES AND ACTIVITY COEFFICIENTS OF THE ALKALI HALIDES

The present investigation involves the measurement of the electromotive forces set up in the following concentration cells without liquid junction:

$$\begin{array}{l} Ag\,|\,AgBr\,|\,NaBr_{M_2}\,|\,Na_xHg\,|\,NaBr_{M_1}\,|\,AgBr\,|\,Ag \\ Ag\,|\,AgBr\,|\,KBr_{M_2}\,|\,K_xHg\,|\,KBr_{M_1}\,|\,AgBr\,|\,Ag \\ Ag\,|\,AgI\,|\,NaI_{M_2}\,|\,Na_xHg\,|\,NaI_{M_1}\,|\,AgI\,|\,Ag \\ Ag\,|\,AgI\,|\,KI_{M_2}\,|\,K_xHg\,|\,KI_{M_1}AgI\,|\,Ag \end{array}$$

where m_1 is approximately 0.1 M. and m_2 varies from 0.01 M. to 3.0 M. From these data the various activity coefficients have been calculated.

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[6] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).
Allmand and Pollack, *J. Chem. Soc.*, **115**, 1020 (1919).
Ming Chow, *J. Am. Chem. Soc.*, **42**, 488 (1920).
MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).
Knobel, *ibid.*, **45**, 70 (1923).
Harned, *ibid.*, **47**, 676, 684, 689 (1925).

[7] Meyer, *Z. physik. Chem.*, **7**, 477 (1891).
Lewis and Kraus, *J. Am. Chem. Soc.*, **32**, 459 (1910).
Lewis and Keyes, *ibid.*, **34**, 119 (1912), **35**, 340 (1913).

The cell, consisting of two separate parts, was of the type developed by Knobel and by Harned but so modified by Akerlof and Swindells[8] as to permit washing without removal from the thermostat. In one limb of each part was placed a silver electrode, and the two symmetrical sections so adjusted as to accommodate the arms of an amalgam dropper in the other limbs. The dropper consisted of a reservoir of about 35 c.c. capacity equipped with two side-arms, by means of which it was evacuated and filled with amalgam, and two capillary arms through which amalgam was allowed to flow into both cell solutions simultaneously.

The solutions to be measured were boiled under reduced pressure, extreme care being taken to prevent access of air, and run into the evacuated cell which was emptied four times and filled finally, to insure complete washing, and allowed to equilibrate for four hours. After this period the amalgam was run into the two solutions, the level of the pools thus formed being kept constant by manipulation of the cell stop-cocks leading into the waste reservoir. During this period continuous electromotive force readings were taken and the average accepted as the voltage of the cell.

It was of utmost importance to exclude all traces of air from the cell solutions in order to prevent decomposition of the amalgam and consequent error in the electromotive force reading. Because of this all solutions had to be boiled, and it was therefore impractical to attempt to obtain exact values of m_1 and m_2. Corrections to round concentrations were made on the assumption that over the small concentration range, the activity coefficients were constant, by the use of the following equations:

$$\Delta E = 0.1183 \log \frac{m_1}{m_0} \qquad \ldots\ldots\ldots (1)$$

$$\Delta E = -0.1183 \log \frac{m_2}{m_0}$$

where m_0 is the desired concentration (0.3, 0.5, 1.0 etc.)

[8] Knobel, *J. Am. Chem. Soc.*, **44**, 70 (1923).
Harned, *ibid.*, **47**, 676 (1925).
Akerlof, *J. Am. Chem. Soc.*, May, 1926.
Swindells, *ibid.*, **48**, 126 (1926).

Table I contains the experimental data, the correction ΔE, the corrected electromotive forces, $E_{corr.}$, the activity coefficients relative to 0.1 M. and the absolute activity coefficient, γ.

TABLE I

ELECTROMOTIVE FORCES AND ACTIVITY COEFFICIENTS OF THE ALKALI HALIDES IN AQUEOUS SOLUTIONS

m_1	m_2	E	ΔE	$E_{cor.}$	$\gamma_2/\gamma_{.1}$	γ_2
		(a) Sodium Bromide				
0.1007	0.01011	0.11019	0.00020	0.11039	1.166	0.903
.1011	.03008	.05763	—.00043	.05720	1.095	.848
.1046	.05065	.03432	—.00165	.03267	1.059	.821
.1000	.1000	.00000	.00000	.00000	1.000	.775
.1010	.3052	.05276	.00051	.05239	.924	.716
.1027	.5038	.07631	.00101	.07732	.901	.698
.1010	1.011	.11239	—.00005	.11234	.890	.689
.1046	1.544	.13374	.00083	.13457	.915	.709
.1015	2.032	.15085	—.00005	.15080	.941	.729
.1021	2.569	.16620	—.00033	.16587	1.009	.782
.1002	3.021	.17818	—.00026	.17792	1.064	.824
		(b) Potassium Bromide				
.1002	.01014	.11172	.00061	.11233	1.123	.865
.1010	.03012	.05657	—.00031	.05626	1.115	.858
.1012	.05060	.03224	.00015	.03239	1.064	.819
.1000	.0000	.00000	.00000	.00000	1.000	.770
.1009	.3028	.05133	—.00002	.05131	.905	.697
.1026	.5158	.07492	—.00028	.07464	.855	.658
.1012	1.007	.10655	.00026	.10681	.799	.615
.1007	1.516	.12584	—.00019	.12565	.769	.592
.1004	2.000	.14081	.00020	.14101	.778	.599
.1010	2.512	.15284	.00027	.15311	.787	.606

m_1	m_2	E	ΔE	Ecor.	$\gamma_2 \mid \gamma_{.1}$	γ_2
		(c) Sodium Iodide				
0.0994	0.01008	0.10916	0.00069	0.10985	1.178	0.919
.1037	.03070	.05791	—.00069	.05722	1.094	.853
.1010	.04957	.03469	—.00098	.03371	1.037	.809
.1000	.1000	.00000	.00000	.00000	1.000	.780
.1008	.3020	.05460	.00009	.05469	.966	.753
.1003	.4970	.07818	.00046	.07864	.924	.721
.0997	1.003	.11500	—.00031	.11519	.988	.771
.1083	2.038	.15683	—.00096	.15999	1.041	.812
		(d) Potassium Iodide				
.1034	.01009	.11226	—.00127	.11099	1.153	.893
.1016	.03079	.05710	.00053	.05763	1.086	.841
.1021	.05158	.03256	—.00051	.03205	1.072	.831
.1000	.1000	.00000	.00000	.00000	1.000	.775
.1008	.3017	.05204	.00015	.05219	.920	.713
.1020	.5103	.07587	—.00004	.07583	.875	.678
.1052	1.017	.10747	.00174	.10921	.837	.649
.0988	2.004	.14532	—.00074	.14458	.834	.646

DISCUSSION OF THE ELECTROMOTIVE FORCES OF THE ALKALI HALIDES

Up to the present, only a few series of accurate data on the electromotive forces of concentration cells without liquid junction containing chlorides, bromides and iodides are available. Pearce and Hart[9] have measured such cells containing potassium bromide which may be compared with the values of MacInnes and Parker[10] on cells containing potassium chloride, or values calculated from the activity coefficient of potassium chloride obtained by other methods. The electromotive forces of similar cells containing hydrochloric acid have been accurately determined in the concentrated solutions,[11] and recently cells containing hydrobromic acid have been measured by Livingston.[12]

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[9] Pearce and Hart, *J. Am. Chem. Soc.*, **43**, 2483 (1921).
[10] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915)
[11] Ellis, *J. Am. Chem. Soc.*, **38**, 737 (1916).
Scatchard, *ibid.*, **47**, 648 (1925), **47**, 2098 (1925).
[12] Livingston, *J. Am. Chem. Soc.*, **48**, 45 (1926).

For the sake of comparison, the electromotive forces of the cells ($m > 0.1$)

$$Ag|AgCl|MCl(m)|M_xHg|MCl(0.1)|AgCl|Ag$$

derived from the data of the above investigators, and the data in Table I have been plotted in Figs. 1 and 2 against log m. In Fig. 1, the plots of solutions of salts of the same cation and different anions are given, and in Fig. 2 are shown the plots of the same anion and different cations. The scale of the ordinates is so selected as to separate the groups of curves in a convenient manner.

The reaction corresponding to the above cell is simply the transfer of the electrolyte from the more concentrated to the dilute solution, namely,

$$MCl(m) = MCl(0.1);\ (-\Delta\overline{F})$$

If $\overline{F}_2$ is the partial free energy in the concentrated solution and $\overline{F}_1$ in the dilute solution,

$$\overline{F}_1 - \overline{F}_2 = -\Delta\overline{F} = E = E_M + E_X$$

since $\overline{F}_2$ is greater than $\overline{F}_1$, and where E_M and E_X are the electromotive forces of transfer of the cation and anion, respectively.

An inspection of the curves reveals their similarity of distribution. Thus, from Fig. 1 it is seen that the electromotive forces are always greater in the order iodide, bromide and chloride, and that the differences between the curves of the potassium salts are approximately the same as those of the sodium salts and of the acids. Further, from Fig. 2, a like similarity is observable, and the differences in electromotive forces between the hydrogen halides and the sodium or potassium halides are approximately the same. This would lead to the conclusion already reached by MacInnes and by Harned[13] that marked additivity relationships exist for the electromotive forces or relative partial free energies

[13] MacInnes, *J. Am. Chem. Soc.*, **41**, 1078 (1919).
Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920).

of these simple ions even in the concentrated solutions. From these results, however, it may be inferred that such additivity is not exactly valid, but approximately so. This point is illustrated in Table II in which the differences in millivolts between successive curves at 1.0 M. concentration, read off large scale plots of the results are given.

TABLE II

DIFFERENCES IN MILLIVOLTS OF ELECTROMOTIVE FORCES OF CELLS CONTAINING HALIDES

KCl	1.6	KBr	2.4	KI
5.2		5.5		5.8
NaCl	2.0	NaBr	2.8	NaI
9.2		9.6		
HCl	2.4	HBr		

Thus the difference between hydrobromic acid and hydrochloric acid is slightly greater than that between sodium bromide and sodium chloride which in turn is greater than that between potassium bromide and potassium chloride. In all cases the differences become greater but only to a slight extent in the cases where the cation has a higher activity coefficient. The same is also observable in the cases where the anion is the same. At 1.58 M., $E_{HBr} - E_{HCl}$: $E_{NaBr} - E_{NaCl}$: $E_{KBr} - E_{KCl}$ as 3.1: 2.7: 2.4, and at 2.0 M., $E_{NaBr} - E_{NaCl}$: $E_{KBr} - E_{KCl}$ as 3.2: 2.6. Further, at 1.58 M., $E_{NaBr} - E_{KBr}$: $E_{NaCl} - E_{KCl}$ as 8.1: 7.8 and $E_{HBr} - E_{NaBr}$: $E_{HCl} - E_{KCl}$ as 15.3: 15.6. Finally, at 3.0 M. $E_{NaBr} - E_{KBr}$: $E_{NaCl} - E_{KCl}$ as 16.2: 15.5.

To sum up, we may say that from these results, the electromotive forces of the halides are approximately additive in the concentrated solutions. Strictly speaking, we infer that the difference in electromotive forces becomes slightly greater in the cases where the ions have the higher electromotive forces or activity coefficients.

There are two other characteristics of these curves which are of importance. In the first place, the electromotive forces of the salts with the common anions increase in the order of the potas-

sium, sodium and hydrogen halides, or the activity coefficient of the electrolyte is greater for the electrolyte yielding the cation of the lowest atomic number. The reverse is true for the electrolytes with the common cation. This is of considerable importance in connection with the development of the theory of behavior of positive contrasted with negative ions. In the second place, the differences in electromotive force when one cation is substituted for another in an electrolytic solution of the same anion, are greater than a similar substitution of an anion in the solution containing the same cation. Thus, at 1.0 M., $E_{NaCl} - E_{KCl}$ is 5.2 millivolts, while $E_{KBr} - E_{KCl}$ is 1.6 millivolts.

ACTIVITY COEFFICIENTS

The activity coefficient ratio, $\frac{\gamma_2}{\gamma_1}$, of the two solutions is derived from the equation:

$$\log \frac{\gamma_2}{\gamma_1} = \frac{E}{.1183} - \log m_2 - 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The electrode reactions taking place are as follows:

$$Na(Na_xHg) = Na^+(m) + E$$

and

$$AgBr = Ag + Br^-(m) - E$$

Adding,

$$Na(Na_xHg) + AgBr = Na^+(m) + Ag + Br^-(m)$$

At two concentrations, m_1 and m_2, the reactions will be

$$Na(Na_xHg) + AgBr = Na^+(m_1) + Ag + Br^-(m_1)$$
$$Na(Na_xHg) + AgBr = Na^+(m_2) + Ag + Br^-(m_2)$$

Subtracting,

$$Na^+(m_1) + Br^-(m_1) = Na^+(m_2) + Br^-(m_2)$$

The equation relating the electromotive forces and activities is

$$E = \frac{RT}{nF} \ln \frac{a^+_{Na}(m_2)\, a^-_{Br}(m_2)}{a^+_{Na}(m_1)\, a^-_{Br}(m_1)}$$

Substituting $\gamma^2 m^2$ for $a_{\overset{+}{Na}} a_{\overline{Br}}$, and evaluating the constants,

$$E = 0.05915 \log \frac{\gamma_2^2 m_2^2}{\gamma_1^2 m_1^2}$$

or

$$E = 0.1183 \log \frac{\gamma_2 m_2}{\gamma_1 m_1}$$

which, when $m_1 = 0.1$, reduces to Equation (2).

These ratios are shown in column six of Table I. In the last column are given the actual activity coefficients of the solutions, using as a basis of calculation, the following values for γ_1 at 0.1 M. concentration:

NaBr	0.775
KBr	.770
NaI	.780
KI	.775

Measurements of 3.0 M. sodium iodide and potassium iodide solutions could not be accurately made because of the increasing solubility of the silver iodide electrodes at the higher concentrations.

DISCUSSION

The values of the activity coefficients of the potassium chloride, bromide and iodide are plotted against the concentration in Fig. 3, and those of the corresponding sodium salts in Fig. 4. These activity coefficients are greater in the order iodide, bromide and chloride. This is a matter of considerable importance for the theory of the behavior of these simple ions.

Thus, the activity coefficients of the halides are greater in the order, hydrogen, lithium, sodium, potassium, etc., or increase with increasing layers of electron shells, which is opposite to the observed results for the electrolytes with the common cation. The underlying cause of this phenomenon is difficult to determine but is probably associated with the fact that the excess negative charge on the halide ions is an outer orbital electron which is

more loosely held by the anion with the largest number of electrons or the anion with the highest nuclear charge. The cations, on the other hand, have their excess charge in the center.

THE ACTIVITY COEFFICIENTS OF SODIUM HYDROXIDE IN SODIUM BROMIDE AND IN SODIUM IODIDE SOLUTIONS

In these measurements the activity coefficients of sodium hydroxide at 0.1 M. concentration in solutions of sodium bromide and sodium iodide at various strengths have been determined by the use of the cells

$$\begin{array}{l} H_2 \,|\, NaOH(m_2) \,|\, Na_xHg \,|\, NaOH(m_1) \,|\, H_2 \\ \qquad NaBr(m) \\ H_2 \,|\, NaOH(m_2) \,|\, Na_xHg \,|\, NaOH(m_1) \,|\, H_2 \\ \qquad NaI(m) \end{array}$$

in which m_1 and m_2 are approximately 0.1 M., and m varies from 0.2 M. to 3.0 M.

The same type of cell was used in these series as in the neutral salt measurements, except that standard hydrogen electrodes replaced the silver electrodes used above. The solutions were made up and boiled and the cell filled, as described above. But after inserting the amalgam dropper, the solutions were allowed to run out of the hydrogen electrode compartments until the electrodes were about half out of water. Hydrogen was now passed in and the cell equilibrated in the usual manner.

Since it was impossible to make m_1 and m_2 exactly the desired value, it was necessary to apply a correction to the observed electromotive force. For this purpose, assuming the activity coefficients to be constant over the small concentration range, the following formula was used:

$$\Delta E = 0.1183 \log \frac{m_1}{0.1} - 0.05915 \log \frac{m_2(m+m_2)}{0.1\,(m+0.1)} \quad \ldots\ldots (3)$$

These concentrations and electromotive force corrections are shown in the first five columns of Table III.

TABLE III

ELECTROMOTIVE FORCES OF CELLS

$H_2|NaBr(m)|NaOH(m_2)|Na_xHg|NaOH(m_1)|H_2$

m_1	m_2	m	E	ΔE	$E_{cor.}$
.1051	.1014	.2068	.02078	.00208	.02286
.1028	.1062	.5315	.03865	—.00037	.03828
.1013	.1001	1.002	.05167	.00064	.05231
.1023	.1016	2.033	.06941	.00073	.07014
.1038	.1045	3.147	.08270	.00075	.08345

$H_2/NaI(m), NaOH(m_2)/Na_xHg/NaOH(m_1)/H_2$

m_1	m_2	m	E	ΔE	$E_{cor.}$
.1025	.1040	.2076	.02271	—.00007	.02264
.1005	.1035	.5123	.03764	—.00017	.03757
.1002	.0994	.984	.05095	.00032	.05127
.0973	.1018	2.032	.07020	.00155	.06865
.0988	.1049	2.994	.08400	—.00184	.08211

The electromotive forces of cells of this type are related to the activities of the electrolyte by the equation:

$$E+0.02568\ln\frac{a_{H_2O(s)}}{a_{H_2O(1)}}=0.05915\log\frac{\gamma Na(s)\gamma\gamma OH(s)\ (m+m_1)}{\gamma Na(m_1)\gamma OH(m_1)} \quad (4)$$

The reactions taking place in the cell are

$$Na(Na_xHg)=Na^+(m)+E$$

and

$$\tfrac{1}{2}H_2(1\text{ atm.})+OH^-(m)=H_2O(1)+E$$

Subtracting, the cell reaction becomes

$$Na(Na_xHg)+H_2O(1)=\tfrac{1}{2}H_2+OH^-(m)+Na^+(m)$$

At two concentrations, m_1 and $(m+m_1)$, the reactions will be

$$Na(Na_xHg)+H_2O(1)=\tfrac{1}{2}H_2+Na^+(m_1)+OH^-(m_1)$$

and

$$Na(Na_xHg)+H_2O(2)=\tfrac{1}{2}H_2+Na^+(m+m_1)+OH^-(m+m_1)$$

By subtraction, we obtain the reaction

$$Na^+(m+m_1)+OH^-(m+m_1)+H_2O(1)=Na^+(m_1)+OH^-(m_1)+H_2O(2)$$

The equation relating the electromotive forces and the activities of the various ionic species is

$$E = \frac{RT}{nF} \ln \frac{a^{+}_{Na}(m+m_1)\ a^{-}_{OH}(m+m_1)\ a_{H_2O}}{a^{+}_{Na}(m_1)\ a^{-}_{OH}(m_1)\ a_{H_2O}}$$

Substituting $\gamma^2 m^2$ for $a^{+}_{Na}a^{-}_{OH}$ and evaluating the constants,

$$E = 0.05915 \log \frac{\gamma_2^1 (m+m_1)^2 a_{H_2O}(1)}{\gamma_1^2, m_1^2, a_{H_2O}(2)}$$

which reduces to Equation (4) above.

Substituting the vapor pressure ratio for the water activity ratio,

$$E + 0.02568 \ln \frac{ps}{p_{.1}} = 0.05915 \log \frac{\gamma Na(s)\gamma OH(s)\ (m+m_1)}{\gamma Na(m_1)\gamma OH(m_1)}$$

Now if the value of $\gamma Na\gamma OH$ of the pure hydroxide is known at the reference concentration, in this case 0.1 M., $\gamma Na(s)\gamma OH(s)$ in the salt solution may be calculated and from this the square root or activity coefficient.

But it is first necessary to evaluate the term, $+0.02568 \ln \frac{p_s}{p_{.1}}$, and add this value to the electromotive force. To do this it is first assumed that the vapor pressure of the solution is the same as if the total concentration were sodium bromide or sodium iodide.

Harned[14] has derived an equation by which the vapor pressure of a salt solution may be calculated:

$$\ln \frac{p_0}{p_s} = \frac{m}{55.5} \left\{ 2 + 2.303 x'_m - \frac{4.606 \beta' m'}{m'+1} m_{m'} \right\}$$

where p_s is the vapor pressure of the solution, and p_0 the vapor pressure of pure water, $_m$ is the concentration and $_{x'}$, β' and $_{m'}$ constants derived from a knowledge of the activity coefficients of the solutes.

[14] Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922).

By transposing the empirical equation derived by Harned

$$\log \gamma = {}_{x}'_{m} - \beta'_{m} m'$$

in which γ is the mean activity coefficient, the formula

$$\left(-\frac{\log \gamma}{m} + {}_{x}'\right) = \beta'_{m} m' - 1$$

is obtained. Taking the logarithms:

$$\log \left(-\frac{\log \gamma}{m} + {}_{x}'\right) = \log \beta' + (m' - 1) \log m.$$

Since the plot of $\left(-\frac{\log \gamma}{m} + {}_{x}'\right)$ against log m should be a straight line, different values were assigned to ${}_{x}'$ until a straight line resulted. m′ was determined from the slope, and β' from the Y − axis intercept. The values of γ were obtained from the preceding neutral salt measurements.

In the sodium hydroxide − sodium bromide series,

$$x' = 0.13 \qquad \beta' = 0.299 \qquad m' = 0.395$$

In the sodium hydroxide − sodium iodide series,

$$x' = 0.09 \qquad \beta' = 0.206 \qquad m' = 0.254$$

From the values of $\ln \frac{p_0}{p_s}$ calculated first at 0.1 M., and then at the total concentrations shown in the table, $\ln \frac{p_s}{p_1}$ was obtained by the relation:

$$\ln \frac{p_0}{p_{.1}} - \ln \frac{p_0}{p_s} = \ln \frac{p_s}{p_{.1}}$$

and finally $0.02568 \ln \frac{p_s}{p_{.1}}$ was evaluated, as shown in Column 3 of Table IV. The final electromotive forces are listed in Column 4 and the absolute values of γ calculated on the basis, $\gamma_{.1} = 0.758$, in Column 5.

TABLE IV

THE ACTIVITY COEFFICIENT OF SODIUM HYDROXIDE IN SODIUM BROMIDE SOLUTIONS

0.1 M. NaOH

m	E	.02568 ln $p_s/p_{.1}$	γ	E+.02568 ln $p_s/p_{.1}$
.0000	.00000	.00000	.758	.00000
.2068	.02286	−.000175	.673	.02269
.5315	.03828	−.000458	.627	.03782
1.002	.05231	−.000894	.621	.05142
2.033	.07014	−.001998	.618	.06815
3.147	.08345	−.003469	.607	.07998

THE ACTIVITY COEFFICIENTS OF SODIUM HYDROXIDE IN SODIUM IODIDE SOLUTIONS

0.1 M. NaOH

m	E	.02568 ln $p_s/p_{.1}$	γ	E+.02568 ln $\frac{p_s}{p_{.1}}$
.0000	.00000	.00000	.758	.00000
.2076	.02264	−.000185	.669	.02246
.5123	.03757	−.000466	.631	.03711
.984	.05127	−.000929	.613	.05034
2.032	.06865	−.002090	.600	.06656
2.994	.08211	−.003326	.571	.07879

SUMMARY

1. Measurements were made of the following types of cells:

(a) $Ag|AgBr|NaBr(m_2)|Na_xHg|NaBr(m_1)|AgBr|Ag$
$Ag|AgBr|KBr(m_2)|K_xHg|KBr(m_1)|AgBr|Ag$
$Ag|AgI|NaI(m_2)|Na_xHg|NaI(m_1)|AgI|Ag$
$Ag|AgI|KI(m_2)|K_xHg|KI(m_1)|AgI|Ag$

(b) $H_2|NaOH(m_2)|Na_xHg|NaOH(m_1)|H_2$
$NaBr(m)$
$H_2|NaOH(m_2)|Na_xHg|NaOH(m_1)|H_2$
$NaI(m)$

2. The activity coefficients of the alkali halides in aqueous solutions have been calculated from these results.

3. It has been found that the electromotive forces of the individual ions of these simple electrolytes are approximately additive in concentrated solutions, when referred to a given concentration.

4. The activity coefficients of sodium hydroxide in solutions of sodium bromide and of sodium iodide have been calculated.

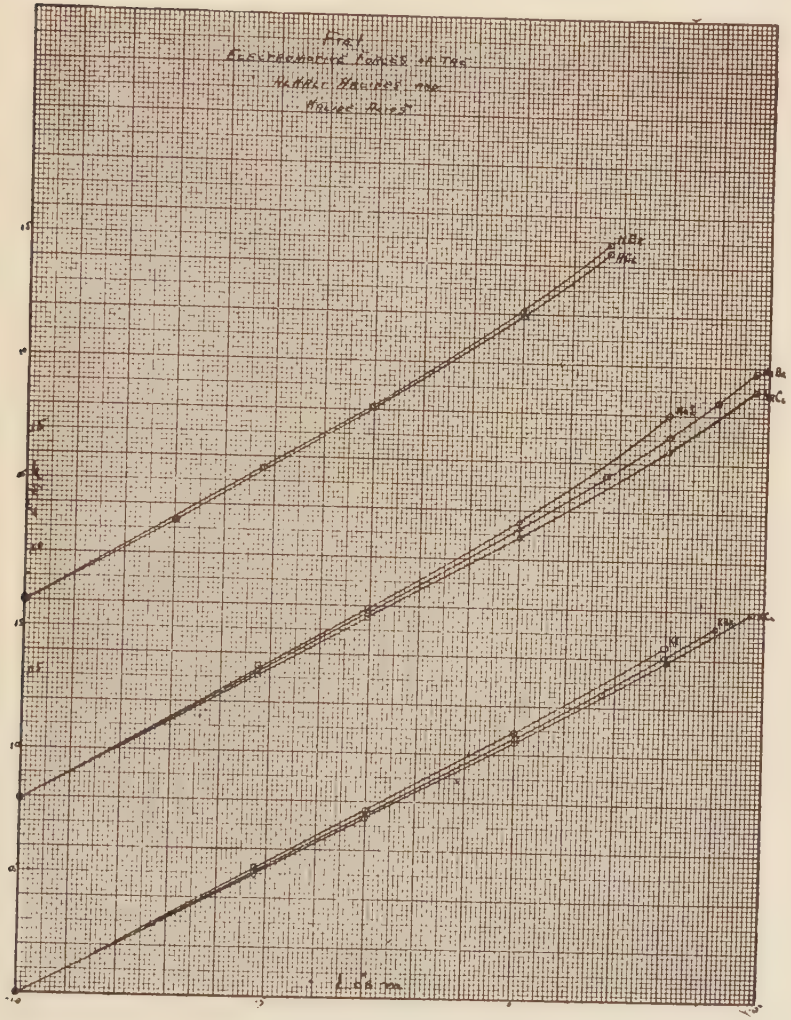
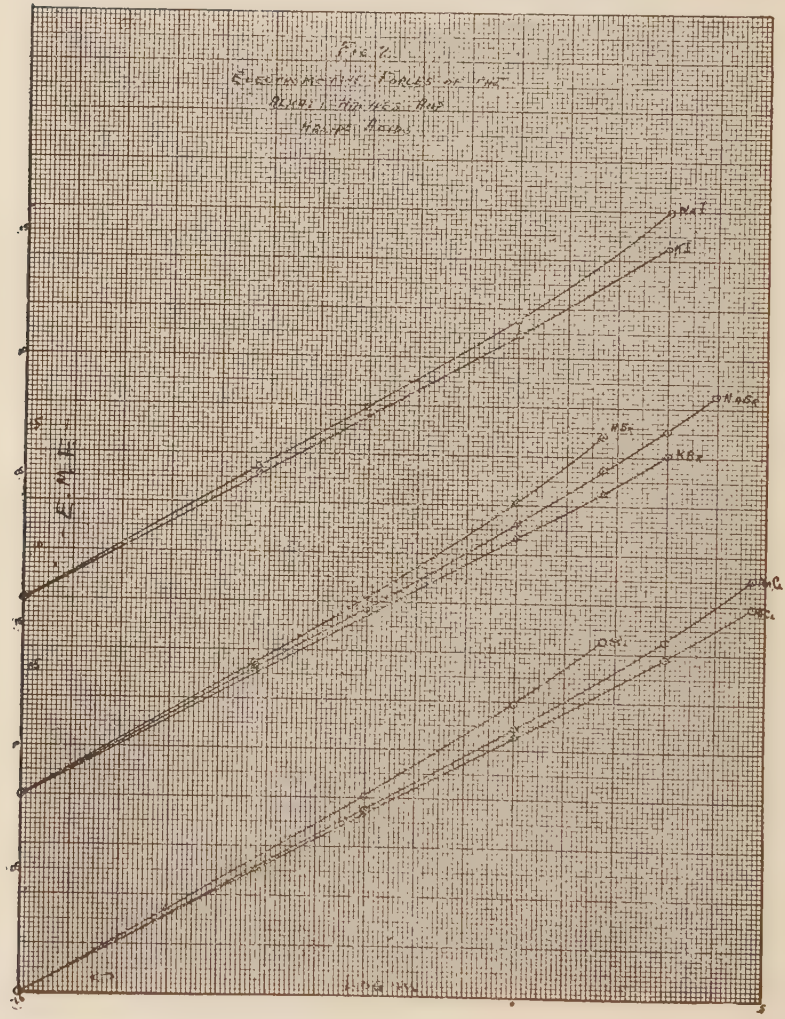


Fig. 1
Electromotive Forces of the
Alkali Halides and
Halide Acids
$\sqrt{m}$


NaI
KI
NaBr
KBr
NaCl
KCl
E.M.F.

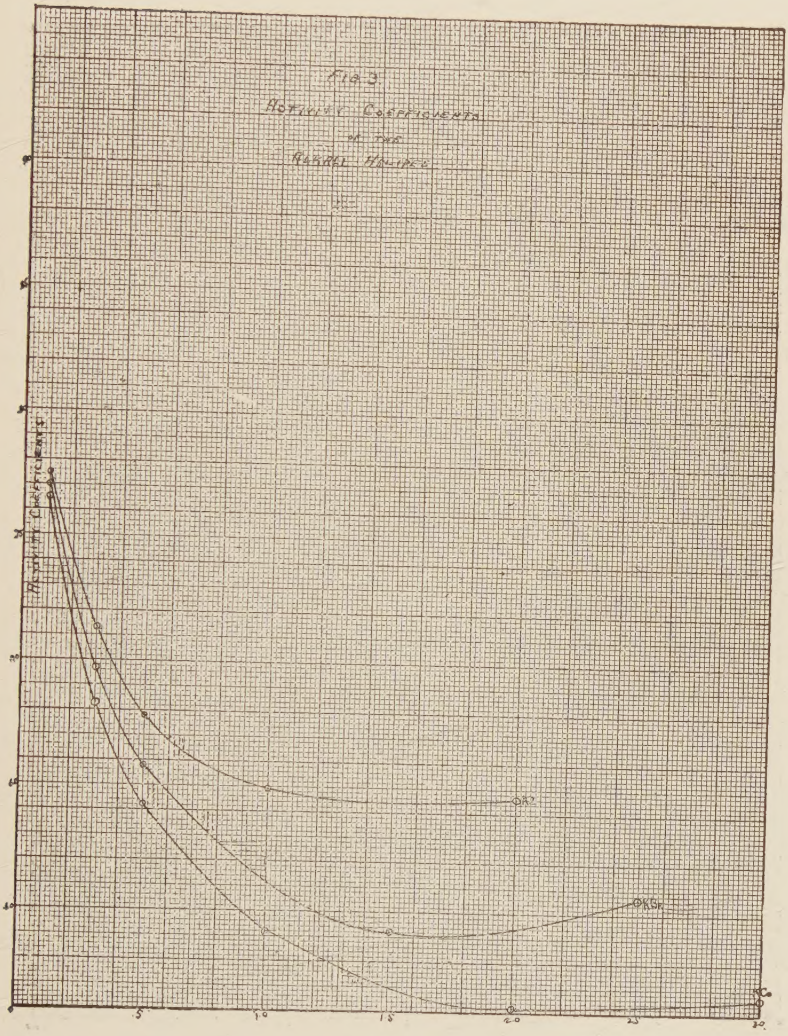


Fig 3
Activity Coefficients
of the
Alkali Halides
Activity Coefficients
5
10
15
20
25
30
°C.
OK?
OKSr

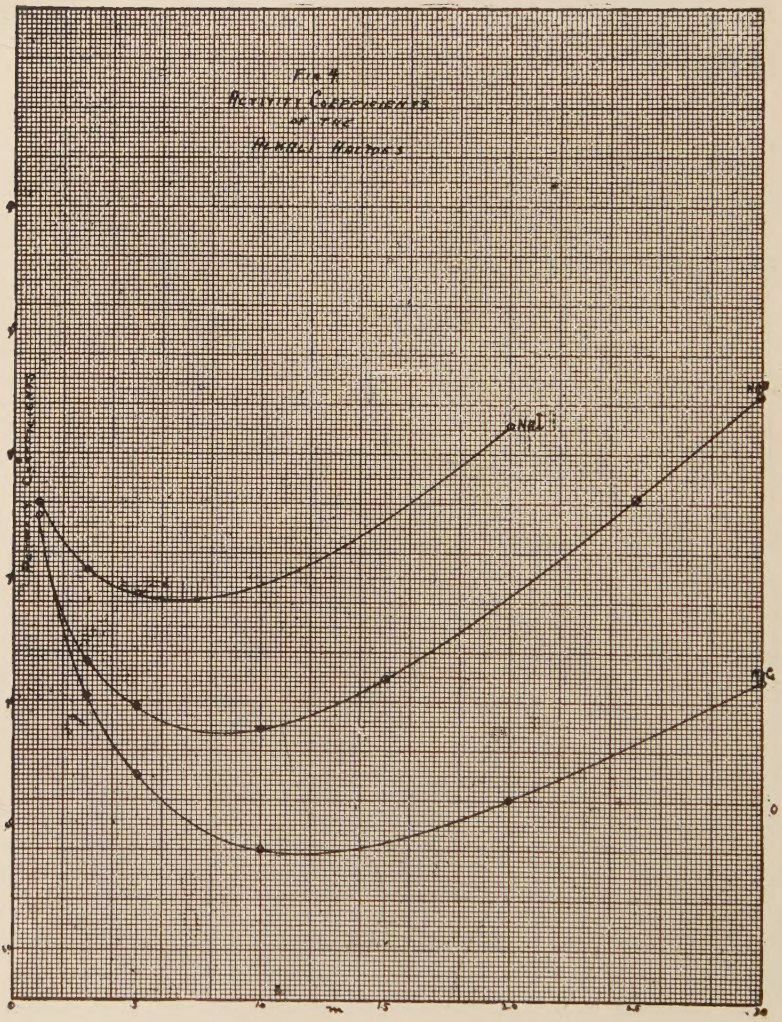


FIG. 4
ACTIVITY COEFFICIENTS
OF THE
ALKALI HALIDES
NaCl
KCl
RbCl
CsCl
0
5
10
15
20
25

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